

Multiple branches of ordered states of polymer ensembles with the Onsager excluded volume potential

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Abstract

We study the branches of equilibrium states of rigid polymer rods with the Onsager excluded volume potential in two-dimensional space. Since the probability density and the potential are related by the Boltzmann relation at equilibrium, we represent an equilibrium state using the Fourier coefficients of the Onsager potential. We derive a non-linear system for the Fourier coefficients of the equilibrium state. We describe a procedure for solving the non-linear system. The procedure yields multiple branches of ordered states. This suggests that the phase diagram of rigid polymer rods with the Onsager potential has a more complex structure than that with the Maier–Saupe potential. A study of free energy indicates that the first branch of ordered states is stable while the subsequent branches are unstable. However, the instability of the subsequent branches does not mean they are not interesting. Each of these unstable branches, under certain external potential, can be made metastable, and thus may be observed.

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The isotropic-nematic phase transition in rigid rod-like polymers is a classical topic [9]. In 1949, Onsager first examined the isotropic-nematic phase transition theoretically by modeling the steric excluded volume interactions [1]. Onsager's study was based on a virial expansion, which yields a mean field potential, now bearing his name (the Onsager potential). Using this mean field potential and choosing an appropriate trial function for the orientation distribution function, Onsager was able to argue that when the concentration is high enough, there is a transition from a uniform isotropic state to an orientationally ordered prolate nematic state. Many theories have been formulated after Onsager's pioneering work. An excellent review on the theoretical advances of liquid crystalline polymers is given in [2]. In this study, we adopt the Doi–Hess model [3,4], which was first developed by Doi and Edwards to describe spatially

homogeneous flows of rodlike liquid crystal polymers and has been used in many studies [5–7]. In the Doi–Hess model, the polymer ensemble is represented by an orientational probability density in a meso-scale much larger than individual polymer rods but much smaller than the macroscopic flow. Each polymer rod undergoes Brownian diffusion and is affected by the interaction with other polymer rods within the meso-scale. The inter-molecular interaction is usually modeled using the Onsager potential or the Maier–Saupe potential, which is an approximation to the Onsager potential. The main mathematical difference between the Onsager potential and the Maier–Saupe potential is that the Onsager potential depends on the whole probability density function while the Maier–Saupe potential depends only on the second moment. As a result, the Doi–Hess model with the Onsager potential is mathematically much more challenging than with the Maier–Saupe potential.

The Doi–Hess model with the Onsager potential has been studied numerically and the Onsager theory has been extended to other systems. For example, Larson [8] applied the spherical

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harmonic expansions to solve the Doi–Hess equation with the Onsager potential for the 3D time-dependent orientation distribution function in the presence of shearing flow. Lasher [10] extended Onsager’s work to the nematic ordering of hard rods with a direct application of the scaled particle approach. Vroege and Lekkerkerker [11] provided a comprehensive overview on the theory and experiments in lyotropic colloidal and polymer liquid crystals. In particular, they generalized Onsager’s virial theory to polydisperse solutions and soft interactions. Chrzanowska [12] developed a simple Onsager theory type density functional theory (DFT) of a two-dimensional system of hard needles.

Recently, the phase diagram of rigid rod polymers with the Maier–Saupe potential, previously obtained in various numerical studies (for example, see [5] and [13] and references therein), has been studied analytically [14–16]. Thus, it is timely and worthwhile to revisit analytically the phase diagram of rigid rod polymers with the Onsager potential. In studying a phase diagram, it is important to get a full picture of the phase diagram, including all stable and unstable branches. Besides mathematical completeness, there are two more reasons for including all branches when studying a phase diagram: (a) the full structure of the phase diagram helps us understand the dynamics and the stabilities; and (b) under a certain external field, unstable branches may be made meta-stable and thus may be observed.

In this Letter, we consider the case of rigid rod polymers in the two-dimensional space with the Onsager intermolecular interaction potential. In the two-dimensional space, orientation is represented by the polar angle θ and the orientational probability density $\rho(\theta, t)$ is governed by the Smoluchowski equation

$$\frac{\partial \rho}{\partial t} = D \frac{\partial}{\partial \theta} \left(\frac{\Phi'_{\text{Onsager}}(\theta)}{k_B T} \rho + \frac{\partial \rho}{\partial \theta} \right), \quad (1)$$

where D is the rotational diffusion coefficient of each polymer rod, k_B the Boltzmann constant and T the absolute temperature. For simplicity, we use $U(\theta)$ to denote the Onsager potential normalized by $k_B T$, which has the form

$$U(\theta) \equiv \frac{\Phi_{\text{Onsager}}(\theta)}{k_B T} = b \int_0^{2\pi} |\sin(\tilde{\theta} - \theta)| \rho(\tilde{\theta}) d\tilde{\theta} = b \int_0^{2\pi} |\sin \tilde{\theta}| \rho(\tilde{\theta} + \theta) d\tilde{\theta}. \quad (2)$$

Here b is proportional to the normalized polymer concentration and is inversely proportional to the temperature. We start with the Fourier expansion of probability density $\rho(\theta)$

$$\rho(\theta) = \frac{1}{2\pi} + \sum_{k=1}^{\infty} (a_k \cos k\theta + b_k \sin k\theta). \quad (3)$$

We first express the Onsager potential in terms of the Fourier coefficients $\{a_k, b_k\}$ of $\rho(\theta)$. For that goal, we first derive two integral identities.

$$\begin{aligned} \int_0^{2\pi} |\sin \tilde{\theta}| \cos k\tilde{\theta} d\tilde{\theta} &= \int_{-\pi}^{\pi} |\sin \tilde{\theta}| \cos k\tilde{\theta} d\tilde{\theta} \\ &= 2 \int_0^{\pi} \sin \tilde{\theta} \cos k\tilde{\theta} d\tilde{\theta} \\ &= \begin{cases} \frac{-4}{k^2 - 1}, & k = \text{even}, \\ 0, & k = \text{odd}, \end{cases} \end{aligned} \quad (4)$$

$$\begin{aligned} \int_0^{2\pi} |\sin \tilde{\theta}| \sin k\tilde{\theta} d\tilde{\theta} &= \int_{-\pi}^{\pi} |\sin \tilde{\theta}| \sin k\tilde{\theta} d\tilde{\theta} \\ &= \int_0^{\pi} \sin \tilde{\theta} \sin k\tilde{\theta} d\tilde{\theta} - \int_0^{\pi} \sin \tilde{\theta} \sin k\tilde{\theta} d\tilde{\theta} = 0. \end{aligned} \quad (5)$$

The Fourier expansion of $\rho(\tilde{\theta} + \theta)$ as a function of $\tilde{\theta}$ has the form

$$\begin{aligned} \rho(\tilde{\theta} + \theta) &= \frac{1}{2\pi} + \sum_{k=1}^{\infty} (a_k \cos k\theta + b_k \sin k\theta) \cos k\tilde{\theta} \\ &\quad + \sum_{k=1}^{\infty} (b_k \cos k\theta - a_k \sin k\theta) \sin k\tilde{\theta}. \end{aligned} \quad (6)$$

Substituting Fourier expansion (6) into Onsager potential (2), and using identities (4) and (5), we obtain the Fourier expansion of $U(\theta)$

$$U(\theta) = \frac{4b}{2\pi} - \sum_{j=1}^{\infty} \left(\frac{4ba_{2j}}{(2j)^2 - 1} \cos 2j\theta + \frac{4bb_{2j}}{(2j)^2 - 1} \sin 2j\theta \right). \quad (7)$$

The equilibrium probability density is related to the Onsager potential by the Boltzmann distribution:

$$\begin{aligned} \rho(\theta) &= \frac{1}{Z} \exp(-U(\theta)), \\ Z &= \int_0^{2\pi} \exp(-U(\theta)) d\theta. \end{aligned} \quad (8)$$

The Boltzmann relation allows us to use the Fourier coefficients of $U(\theta)$ to represent the equilibrium state. For that purpose, we introduce

$$c_{2j} = \frac{4ba_{2j}}{(2j)^2 - 1}, \quad d_{2j} = \frac{4bb_{2j}}{(2j)^2 - 1}. \quad (9)$$

In terms of $\{c_{2j}, d_{2j}\}$, $U(\theta)$ and $\rho(\theta)$ have the expressions:

$$U(\theta) = \frac{4b}{2\pi} - \sum_{j=1}^{\infty} (c_{2j} \cos 2j\theta + d_{2j} \sin 2j\theta), \quad (10)$$

$$\begin{aligned}\rho(\theta) &= \frac{1}{Z} \exp(-U(\theta)) \\ &= \frac{1}{Z} \exp\left(\sum_{j=1}^{\infty} (c_{2j} \cos 2j\theta + d_{2j} \sin 2j\theta)\right)\end{aligned}\quad (11)$$

where Z is the partition function given by

$$Z = \int_0^{2\pi} \exp\left(\sum_{j=1}^{\infty} (c_{2j} \cos 2j\theta + d_{2j} \sin 2j\theta)\right) d\theta.$$

Eq. (11) shows that the equilibrium probability density $\rho(\theta)$ is periodic with period π . Consequently, in the Fourier expansion of $\rho(\theta)$, we have $a_{2j+1} = b_{2j+1} = 0$.

Next we show that $U(\theta)$ can be made an even function by shifting the coordinate system. Using (9) to relate $\rho(\theta)$ given in (3) to the derivatives of $U(\theta)$ given in (10), we get

$$\begin{aligned}\rho(\theta) &= \frac{1}{2\pi} + \sum_{j=1}^{\infty} (a_{2j} \cos 2j\theta + b_{2j} \sin 2j\theta) \\ &= \frac{1}{2\pi} + \frac{1}{4b} \sum_{j=1}^{\infty} (c_{2j}((2j)^2 - 1) \cos 2j\theta \\ &\quad + d_{2j}((2j)^2 - 1) \sin 2j\theta) \\ &= \frac{1}{4b} (U''(\theta) + U(\theta)).\end{aligned}\quad (12)$$

Combining this result with the Boltzmann relation (8) leads to a non-linear differential equation for the Onsager potential $U(\theta)$:

$$U''(\theta) + U(\theta) - \frac{4b}{Z} \exp(-U(\theta)) = 0. \quad (13)$$

Let θ_0 be the location where $U(\theta)$ attains its maximum in $[0, 2\pi]$. We shift the coordinate system to make $\theta_0 = 0$. Thus, the initial conditions for differential equation (13) at $\theta = 0$ are $U(0) = U_0$ and $U'(0) = 0$. Both the differential equation and the initial conditions are invariant under the change of variable $\theta_{\text{new}} = -\theta_{\text{old}}$. Therefore, we conclude that $U(\theta) = U(-\theta)$, and consequently $d_{2j} = 0$. It follows from (9) that $b_{2j} = 0$. In terms of $\{c_{2j}\}$, $U(\theta)$ and $\rho(\theta)$ have the expressions:

$$U(\theta) = \frac{4b}{2\pi} - \sum_{j=1}^{\infty} c_{2j} \cos 2j\theta, \quad (14)$$

$$\rho(\theta) = \frac{1}{\int_0^{2\pi} \exp(\sum_{j=1}^{\infty} c_{2j} \cos 2j\theta) d\theta} \exp\left(\sum_{j=1}^{\infty} c_{2j} \cos 2j\theta\right) \quad (15)$$

(9) is one set of equations relating Fourier coefficients $\{a_{2j}\}$ and $\{c_{2j}\}$. Calculating Fourier coefficients $\{a_{2j}\}$ directly from $\rho(\theta)$ expressed in (15) yields a second set of equations relating $\{a_{2j}\}$ and $\{c_{2j}\}$:

$$\begin{aligned}a_{2k} &= \frac{1}{\pi} \int_0^{2\pi} \cos 2k\theta \rho(\theta) d\theta \\ &= \frac{1}{\pi} \frac{\int_0^{2\pi} \cos 2k\theta \exp(\sum_{j=1}^{\infty} c_{2j} \cos 2j\theta) d\theta}{\int_0^{2\pi} \exp(\sum_{j=1}^{\infty} c_{2j} \cos 2j\theta) d\theta}.\end{aligned}\quad (16)$$

Combining (9) and (16), we arrive at a non-linear system for $\{c_{2k}\}$.

$$\begin{aligned}\frac{\int_0^{2\pi} \cos 2k\theta \exp(\sum_{j=1}^{\infty} c_{2j} \cos 2j\theta) d\theta}{\int_0^{2\pi} \exp(\sum_{j=1}^{\infty} c_{2j} \cos 2j\theta) d\theta} \\ = \frac{\pi}{4b} (4k^2 - 1) c_{2k}, \quad k = 1, 2, 3, \dots.\end{aligned}\quad (17)$$

Below we describe a procedure for solving non-linear system (17). Here, we use the Fourier coefficients $\{c_{2j}\}$ of $U(\theta)$ to represent an equilibrium state. The equilibrium probability density $\rho(\theta)$ is related to $U(\theta)$ by the Boltzmann distribution and is expressed in terms of $\{c_{2j}\}$ in (15). The advantage of using Fourier coefficients $\{c_{2j}\}$ and the exponential form (15) is that the positivity of equilibrium probability density $\rho(\theta)$ is automatically enforced without putting any constraints on the Fourier coefficients $\{c_{2j}\}$.

We solve non-linear system (17) for ordered states. Here an ordered state is one in which not all the coefficients of $\{c_{2j}\}$ are zero. We first find ordered states with $c_2 \neq 0$. In non-linear system (17), b is a physical parameter that can be tuned by varying the polymer concentration or the temperature. From the point of view of physics, it is desirable to express (c_2, c_4, c_6, \dots) , the solution of nonlinear system (17), as a function of b . Mathematically, however, it is more convenient to treat c_2 as an independent variable and view b as a function of c_2 . We adopt this mathematical formulation. Specifically, in non-linear system (17), we let $r \equiv c_2$, we treat r as a parameter, and we solve for b and (c_4, c_6, c_8, \dots) . The iterative procedure described below provides a way of constructing solution b and (c_4, c_6, c_8, \dots) for a given value of $c_2 = r \neq 0$. For conciseness of presentation, we introduce shorthand notations. Let $\mathbf{C} \equiv (c_4, c_6, c_8, \dots)$. Remember c_2 is fixed at the given value of r . We introduce functions:

$$\begin{aligned}\chi_{2k}(\mathbf{C}) &\equiv \frac{\int_0^{2\pi} \cos 2k\theta \exp(r \cos 2\theta + \sum_{j=2}^{\infty} c_{2j} \cos 2j\theta) d\theta}{\int_0^{2\pi} \exp(r \cos 2\theta + \sum_{j=2}^{\infty} c_{2j} \cos 2j\theta) d\theta}, \\ k &= 1, 2, 3, \dots.\end{aligned}\quad (18)$$

With these notations, non-linear system (17) becomes

$$\frac{3\pi}{4b} r = \chi_2(\mathbf{C}), \quad (19)$$

$$\frac{(4k^2 - 1)\pi}{4b} c_{2k} = \chi_{2k}(\mathbf{C}), \quad k = 2, 3, 4, \dots. \quad (20)$$

Suppose the n th iteration starts with $\mathbf{C}^{(n)} = (c_2^{(n)}, c_4^{(n)}, c_6^{(n)}, c_8^{(n)}, \dots)$. Remember that, in our mathematical formulation, $c_2 = r \neq 0$ is given while b is part of the solution to be determined. So we use Eq. (19) to update b and then use Eq. (20) to update the rest of the Fourier coefficients (c_4, c_6, c_8, \dots) .

$$\text{Update } b: \quad b^{(n+1)} = \frac{3\pi}{4\chi_2(\mathbf{C}^{(n)})} r,$$

$$\text{Update } c_{2k}: \quad c_{2k}^{(n+1)} = \frac{4b^{(n+1)}}{(4k^2 - 1)\pi} \chi_{2k}(\mathbf{C}^{(n)}), \\ k = 2, 3, 4, \dots$$

Our iterative procedure $\mathbf{C}^{(n)} \rightarrow \mathbf{C}^{(n+1)}$ is

$$c_{2k}^{(n+1)} = \frac{3r}{(4k^2 - 1)\chi_2(\mathbf{C}^{(n)})} \chi_{2k}(\mathbf{C}^{(n)}), \quad k = 2, 3, 4, \dots \quad (21)$$

This is how we calculate the first branch of ordered state. The convergence of iterative method (21) is verified in numerical implementations. A rigorous mathematical proof for the convergence, however, is still open.

Next we calculate the second branch of ordered states by finding solutions of (17) with $c_2 = 0$ but $c_4 \neq 0$. Specifically, in non-linear system (17), we keep $c_2 = 0$, we keep $c_4 \neq 0$ fixed and treat it as a parameter, and we solve for b and $(c_6, c_8, c_{10}, \dots)$. One way to keep $c_2 = 0$ is to assume that solutions on the second branch have $2 \times 2 = 4$ fold symmetry, that is, they are periodic with period $2\pi/4$. If $g(\theta)$ is periodic with period $2\pi/4$, then we always have $\int_0^{2\pi} \cos 2\theta g(\theta) d\theta = 0$. Our numerical calculations indicate that invoking symmetry is the only way to keep $c_2 = 0$, although a rigorous mathematical proof is still open. With the 4 fold symmetry, we only need to consider the Fourier coefficients $\{c_{4j}, j \geq 1\}$. Recall that in our mathematical formulation, we keep the leading non-zero Fourier coefficient fixed and treat it as a parameter. For the second branch, we keep $c_4 \neq 0$ fixed and treat it as a parameter. Then, the resulting non-linear system for b and $\{c_{4j}, j > 1\}$ is solved using an iterative procedure similar to (21) described above. The subsequent branches of ordered states are calculated in a similar way. For example, the third branch is calculated by invoking $2 \times 3 = 6$ fold symmetry.

To plot the phase diagram, we represent an ordered state using the magnitude of the Onsager potential, $\sqrt{\sum_{j=1}^{\infty} (c_{2j})^2}$. Fig. 1(a) shows the first three branches of ordered states of rigid rod polymers with the Onsager potential. The first branch (labeled as $S_1(b)$) intersects with the isotropic state at $b \approx 4.7124$. The second branch (labeled as $S_2(b)$) intersects with the isotropic state at $b \approx 23.5619$. The third branch (labeled as $S_3(b)$) intersects with the isotropic state at $b \approx 54.9779$. The procedure of calculating ordered states can be continued beyond the first three branches shown. Numerical results suggest that there are infinitely many branches of ordered states where the k th branch is characterized by having $2k$ -fold symmetry with $c_{2k} = 0$ but $c_{4k} \neq 0$. For this reason, in the space of $\{c_{2j}, j = 1, \dots, \infty\}$, which is of infinite dimensions, two different branches of ordered states will never intersect each other. Interestingly, in the two-dimensional space of $(b, \sqrt{\sum_{j=1}^{\infty} (c_{2j})^2})$, as shown in Fig. 1(a), it is also true that two different branches of ordered states will not intersect each other.

In comparison, in the case of polymers with the Maier-Saupe intermolecular potential, there is only one branch of ordered states and it intersects with the isotropic state at $b = 4$. Fig. 1(b) compares the only branch of ordered states for the Maier-Saupe polymer (dashed line) with the first branch of ordered states for the Onsager polymers (solid line).

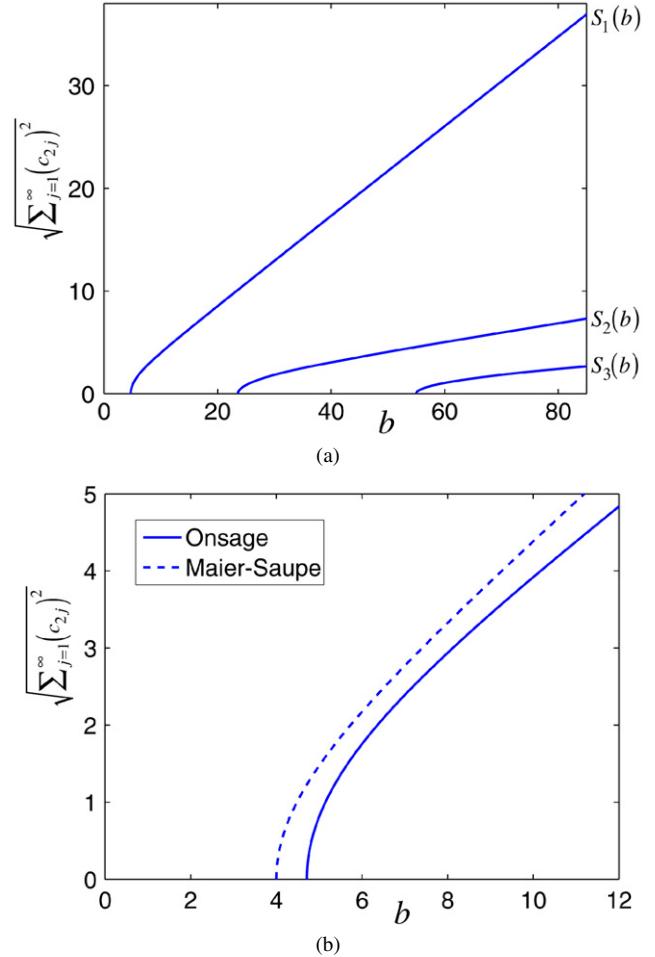


Fig. 1. (a) The first three branches of ordered state for the Onsager polymer. (b) The comparison of the only branch of ordered states for the Maier-Saupe polymer (dashed line) with the first branch of ordered states for the Onsager polymers (solid line).

In the numerical calculation above, we used $\{c_{2j}, j = 1, \dots, N\}$ with $N = 4096$. The infinite sum $\sqrt{\sum_{j=1}^{\infty} (c_{2j})^2}$ is approximated by the corresponding partial sum. To show that this approach is at least self-consistent and that $N = 4096$ is large enough, we examine how fast $|c_{2j}|$ converges to zero as j increases. Fig. 2(a) shows the plot of $|c_{2j}|$ vs index j for the solution on the first branch at $b = 80$. It is clear that as j increases, $|c_{2j}|$ decays exponentially to zero, and the limit of machine precision is reached at about $j \approx 500$.

To determine the stability of the branches of ordered states shown in Fig. 1(a), we examine the free energies of these equilibrium states. The Onsager free energy functional of probability density $\rho(\theta)$ at normalized polymer concentration b is given by

$$G([\rho], b) \equiv \int_0^{2\pi} \left(\rho(\theta) \ln \rho(\theta) + \frac{1}{2} U(\theta) \rho(\theta) \right) d\theta. \quad (22)$$

Fig. 2(b) shows the free energies of the isotropic branch (dashed line) and the first three branches of ordered states (solid lines) for the Onsager polymers. More detailed studies of free

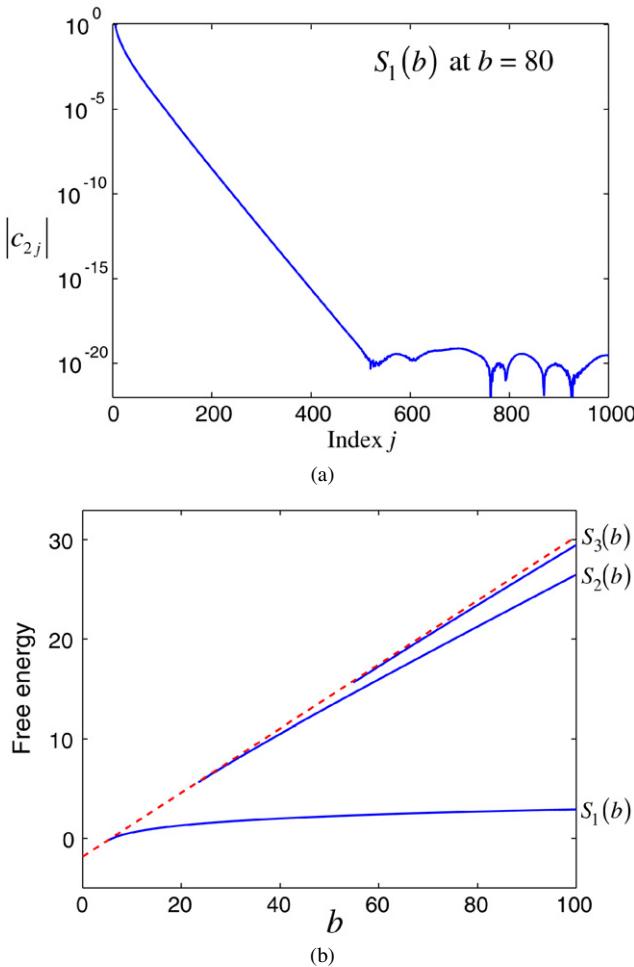


Fig. 2. (a) Plot of $|c_{2j}|$ vs index j . (b) Free energies of the isotropic branch (dashed line) and the first three branches of ordered states (solid lines) for the Onsager polymers.

energies reveal that the isotropic branch is stable before the first branch of ordered states appears (i.e., for $b < 4.7124$). Once the first branch of ordered states appears (i.e., for $b > 4.7124$), the isotropic branch becomes unstable. The first branch of ordered states is stable while the subsequent branches ordered states are unstable. The instability of the subsequent branches of ordered states does not mean these branches are not interesting. For example, the second branch of ordered states can be made metastable under an external potential of the form $\Phi_{\text{External}}(\theta) = A \cos 4\theta$, and thus may be experimentally observed under such a condition.

In [17], the equilibrium bifurcation map of 3D polymers with the Onsager interaction potential was studied. A linear stability analysis of the base isotropic state was carried out. It was found that high order bifurcations are linearly unstable. Our results on 2D polymers with the Onsager interaction potential are consistent with the 3D results in [17]. In a future study, we will (a) tackle the mathematical conjectures suggested by numerical calculations; and (b) carry out asymptotic analysis to identify the exact bifurcation locations and find asymptotic expansions of branches near bifurcation locations. One of our goals is to first re-derive all conclusions in the 2D case ana-

lytically so that all conclusions are established on solid mathematical ground. Once the 2D case of the Onsager polymers is analytically solved, we will move on to revisit the 3D case analytically. For the 3D case of the Onsager polymers, we shall start with a rigorous mathematical derivation of the axisymmetry. The axisymmetry of equilibria of the 3D Maier–Saupe polymers has been mathematically established only recently in three studies [14–16]. All these three studies rely heavily on the specific form of the Maier–Saupe potential. For analytical studies of the 3D Onsager polymers, new mathematical tools are needed.

The multiple branches of ordered states for the Onsager polymers stem from the fact that the Fourier expansion of function $|\sin \theta|$, the kernel in the Onsager potential, has infinite number of terms.

$$|\sin \theta| = \frac{2}{\pi} - \sum_{k=1}^{\infty} \frac{4}{\pi(4k^2 - 1)} \cos 2k\theta. \quad (23)$$

The solutions on the k th branch have $2k$ fold symmetry. Basically, in every meso-scale neighborhood (since we are studying spatially homogeneous solutions) the ensemble of polymer rods is divided into k sub-groups of equal size, and each sub-group is aligned with a director. The k directors are uniformly spaced on the unit circle, resulting in a $2k$ fold symmetry. This $2k$ fold symmetry of the k th branch corresponds to the terms $\cos 2k\theta$, $\cos 4k\theta$ and beyond in the Onsager potential (23). Indeed, for an ensemble of polymer rods with the Onsager interaction potential, if k sub-groups and k directors are sustained by an external force, then a newly added polymer rod will align with any of these k directors individually with equal probability. Again, a newly added polymer rod is able to see these k directors individually because of the terms $\cos 2k\theta$, $\cos 4k\theta$ and beyond in the Onsager potential (23). In the Maier–Saupe potential, however, the kernel is replaced by $-\cos^2 \theta = \text{const} - \frac{1}{2} \cos 2\theta$, which has only the $\cos 2\theta$ term in its Fourier expansion (excluding the constant term). As a result, the $2k$ fold symmetry is suppressed for $k > 1$. For an ensemble of polymer rods with the Maier–Saupe interaction potential, even if k sub-groups and k directors are sustained by an external force, a newly added polymer rod will not be able to see the k directors individually for $k > 1$. That is why the polymers with the Maier–Saupe potential have only one branch of ordered states.

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